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ALKALINE EARTH-NOBLE GAS EXCIMERS.(U)
AUG 81 J J WRIGHT F49620-79-C-0049
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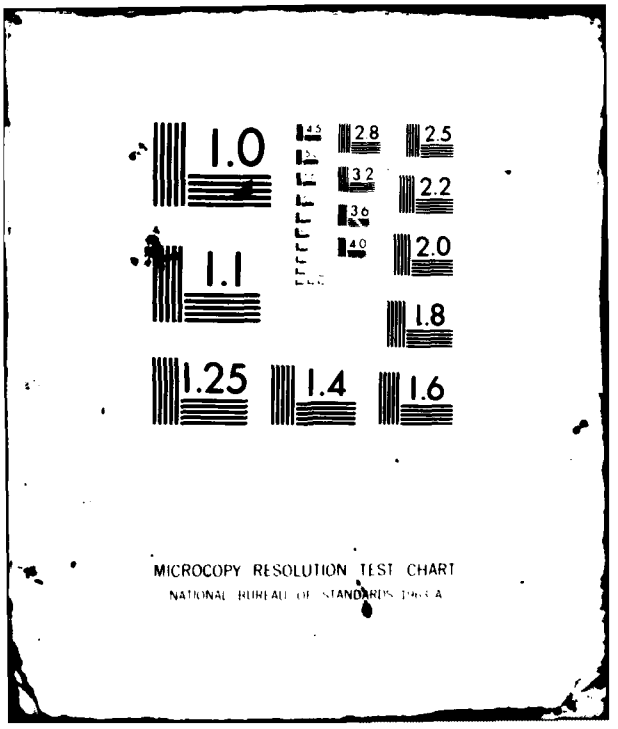
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This project was undertaken to investigate the interaction between alkaline earth atoms in the triplet state and noble gas atoms. A major effort was devoted to producing large triplet state populations via laser excitation of the singlet state and collisional transfer to the triplet state. Cross sections for this process were measured using a new technique developed in this laboratory. These cross sections were much larger than expected, probably due to molecular curve crossings with intermediate states.

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The results predicted a population inversion in strontium was possible and an attempt was made to produce a strontium laser. Because of low laser pump power, an inversion of only fifty percent was achieved where as lasing threshold required ninety percent.

Attempts to observe far wing emission from calcium and strontium interactions with noble gases at high temperatures failed because of the thermal energies involved and because of blackbody radiation. A technique was developed to do laser spectroscopy at low temperatures in a sealed cell containing metal atom vapors and high pressure noble gases. The technique was tested by measuring, for the first time, the excited state potential of the sodium-helium excimer molecule. This difficult experiment was made possible by state of the art laser spectroscopy and the low temperature technique, which enhanced the excimer emission by orders of magnitude.

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FINAL TECHNICAL REPORT

TITLE: Alkaline Earth-Noble Gas Excimers

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INCLUSIVE DATES: 1 March 1979 - 31 August 1981

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RESEARCH PERSONNEL: Dr. L.C. Balling
Dr. M.D. Havey
Paul Fletcher
Steve Frolking

PUBLICATIONS:

"$^1P_1 \rightarrow {}^3P_1$ Excitation Transfer for Ca and Sr with the Noble Gases", J.J. Wright and L.C. Balling, J. Chem. Phys. 73, 1617 (1980).

"Experimental Potentials of the $X^2\Sigma^+$ and $A^2\Pi$ States of NaHe", M.D. Havey, S.E. Frolking, and J.J. Wright, Phys. Rev. Letters 45, 1783 (1980).

"Experimentally Determined Potential Curves for the $X^2\Sigma^+$ and $A^2\Pi$ States of NaNe", M.D. Havey, S.E. Frolking, J.J. Wright and L.C. Balling, accepted for publication in Phys. Rev.

"$A^2\Pi$ Potentials of LiHe and LiNe", J.J. Wright, M.D. Havey, and L.C. Balling, to be submitted for publication.

PRESENTATIONS:

"Ca and Sr $^1P_1 \rightarrow {}^3P_1$ Excitation Transfer", AFOSR Contractors' Meeting, Colorado Springs, Oct. 1979.

"Noble Gase Collision Induced $^1P_1 \rightarrow {}^3P_1$ Excitation Transfer in Ca and Sr", Annual APS DEAP Meeting, Houston, Bull. Am. Phys. Soc. 24, 1177 (1979).

"Laser Spectroscopy of Van der Waals Molecules at Low Temperatures", Seminar at AFWL, Kirtland AFB, July, 1980.

"Experimental Potentials for the NaHe Molecule", AFOSR Contractors' Meeting, Hanscom AFB, Oct. 1980.

Experimental Potential Curves for the $X^2\Sigma^+$ and $A^2\Pi$ State of NaNe", APS Meeting, Baltimore, Bull. Am. Phys. Soc. 26, 596 (1981).

RESEARCH OBJECTIVES:

The major objective of this program is to investigate excimer molecules which are potential laser candidates, primarily excimers formed from Group IIA metal atoms in the metastable ^3P state. These metastable atoms are particularly attractive excimer candidates for several reasons. The ^3P states are low lying electronic levels and so should give excimer emission in the visible or near infrared. These metastable atoms can be produced with high efficiency in a chemical reaction, allowing for the possibility of a chemically pumped excimer laser. And finally, because of the long lifetimes of these states, they offer the potential for an efficient energy storage system.

STATUS OF RESEARCH EFFORT:

I. Excitation Transfer Measurements

Our initial efforts were directed towards producing large populations of atoms in the metastable ^3P state of Ca and Sr. Direct laser excitation is inefficient because of the small oscillator strength for the $^1S_0 \rightarrow {}^3P_1$ transition. However, we found that we could produce over 50% of the atoms in the ^3P state by laser pumping the resonance line of Ca and Sr ($^1S_0$-$^1P_1$) and then transferring the energy to the ^3P state via collisions with rare gas atoms. We developed a new technique for making these measurements which does not depend upon the amount of radiation trapping of the resonance line. Using an N_2 laser-pumped dye laser with 6 ns pulses to pump the ^1P state, a 1/4 m spectrophotometer and fast oscilloscope, we were able to observe the time-resolved fluorescence from both the ^1P and ^3P states.

The fluorescence intensity integrated over time yields the ratio of atoms in the triplet state to those which radiatively decay from the singlet state. This information, along with the measured decay rate of the ^1P state, is sufficient to calculate a transfer rate at a particular noble gas density. Fig. 1 shows some typical plots of the transfer rate as a function of noble gas density for Ca and Sr with several noble gases. Table I lists the measured cross sections for $^1P \rightarrow {}^3P$ excitation transfer. These large cross sections imply that a few atmospheres of noble gas should give transfer times on the order of one nanosecond. Since the noble gases do not quench the $^3P_1$ states and these states live for times greater than 60 μs, pumping the $^1P_1$ resonance line with an intense laser could produce a population inversion between the metastable $^3P_1$ state and the $^1S_0$ ground state.

II. Sr Laser

We attempted to make a Sr laser using Kr gas as the transfer agent. Our laser cell consisted of a 36 cm long stainless steel cell with Brewster windows on the ends and a small side arm port to view the fluorescence. The cavity was a folded confocal configuration made of a 100% reflecting flat and a 1 meter radius of curvature mirror coated to reflect 99.9% at 6890 Å ($^3P_1 \rightarrow {}^1S_0$) and transmit 95% at 4607 Å ($^1S_0 \rightarrow {}^1P_1$). The Sr cell contained two atmospheres of Kr gas and was heated to 600°C ($\sim 10^{-1}$ Torr Sr). The $^1P_1$ state was pumped using a Phase-R flashlamp-pumped dye laser ($\sim$ 0.1 J per pulse) which made two passes through the cell because of the 100% cavity mirror. We tried to detect lasing action by observing the $^3P_1$ fluorescence through the small port perpendicular to the laser cavity. No

evidence of lasing was ever detected. We concluded our pump laser was not intense enough to achieve the necesssary inversion.

To monitor the fractional population of Sr atoms in the $^3P_1$ state we devised the scheme shown in Fig. 2. We pumped the $^1P_1$ state with the Phase-R laser. A trigger pulse from this laser was delayed and then used to trigger the N_2 laser-pumped dye laser also tuned to the resonance line ($^1S_0$-$^1P_1$). This probe pulse was focused into the Sr cell colinear with the Phase-R laser pulse but delayed in time. The fluorescence from the $^1P_1$ state was monitored as a function of the delay time. (The $^3P_1$ lifetime is $\sim$ 60 μs.) From the relative fluorescence amplitudes we were able to conclude that we were depleting 50% of the ground state Sr population; i.e., one half of the Sr atoms were in the ^3P state. To achieve inversion we need 90% in the ^3P state. Since the $^3P_2$ and $^3P_0$ are in equilibrium with the $^3P_1$, only about 1/3 of the atoms are in the $^3P_1$ state. There is another factor of 3 because of the degeneraries of the $^3P_1$ and $^1S_0$ states. With a more intense pump laser, inversion is possible.

III. Sr-Rare Gas Excimers (Preliminary Search)

We have made preliminary searches for SrXe and SrKr excimer fluorescence. Using the pulsed dye laser to excite the $^1P_1$ state and collisional transfer to populate the $^3P_1$ state, we searched the entire visible spectrum and the infrared spectrum to 10,000 Å but were not able to detect any red wing emission on the $^3P_1$ state. Because of the pulsed nature of our laser and black body radiation from our sample oven, we could not have seen any red wing emission less than 10^{-3} that of the $^3P_1$ fluorescence. In order to overcome the problems of black body radiation and weak emission intensities

we devised a new technqiue. At low temperatures there is no black body radiation while the red wing emission increases exponentially. To test the technique we decided to look for emission from NaHe molecules. This choice was made because of the theoretical interest in NaHe and because we could use the cw dye laser.

IV. NaHe and NaNe Excimer Potential Curves

There is considerable disparity among the theoretical results for the NaHe $A^2\Pi$ state well depth and equilibrium radius, ranging from 32 cm^{-1} at 6.2 a_o to 970 cm^{-1} at 3.0 a_o. The only experimental study to yield direct information on the $A^2\Pi$ is a far wing line broadening measurement. This experiment yielded a well depth less than 20 cm^{-1} for NaNe, which has since been theoretically and experimentally determined to be about 150 cm^{-1}. This put into serious question the reliability of the NaHe results. If the well depth is large and the minimum occurs at small Na-He internuclear separation, the NaHe molecular system would potentially be a good metal vapor system.

We have observed the temperature dependence of the far wing of the 3s-3p transition of Na (broadened by He and Ne) in the range 100°K-300°K. A bulb containing 600-1000 Torr of He is cooled with cold N_2 gas. A side arm containing Na is heated to produce a Na density in the 10^{-7}-10^{-6} Torr range in the central region of the bulb. The Na 3s-3p resonance line is excited with a cw dye laser and the far wing fluorescence measured with a 1/2 m spectrometer. Fig. 3 is a schematic diagram of the basic experimental setup.

Representative plots of our temperature dependent data are shown in Fig. 4. Our results for the $A^2\Pi$ state potential of NaHe and NaNe are shown in Figs. 5 and 6. Our experimental values for the well depths are 480 cm^{-1} at 4.4a_o and 160 cm^{-1} at 5.1a_o in NaHe and NaNe, respectively.

V. LiHe Excimer Potentials

Because of its lower vapor pressure, high reactivity with glass, and red emission, the problems encountered with Li more nearly approximate those of Group II metals. To prevent reaction with the glass, the Li metal was put into an iron boat which had a stainless steel sleeve. The sleeve was necessary to have the Li metal creep up to the mouth of the boat. The 250 ml Pyrex cell had a quartz tip to hold the iron boat. Quartz was necessary because the tip temperature is typically 600°C (Fig. 3). Fig. 7 shows the enhancement in wing intensity as the cell temperature is reduced from 100°C to -100°C. Preliminary results yield an $A^2\Pi$ potential well depth of 850 cm^{-1}, in good agreement with recent theoretical calculations. It is intended to complete the LiHe measurements and to measure the LiNe $A^2\Pi$ state potential.

VI. Search for BaHe Excimer Emission

A BaHe cell was made similar to the Li-He cell with the Ba in a stainless steel lined iron boat. Using cw dye laser excitation, good $^1P_1$-$^1S_0$ resonance fluorescence signals were observed in the presence of ~300 Torr He. No red wing emission was detected under conditions where LiHe and NaHe emissions were easily observed.

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It is proposed that the rapid $^1P_1 \rightarrow {}^3P_1$ transfer in Ca and Sr is due to molecular curve crossings since $^1D_2$ and ^3D_J states exist between the

$^1P_1$ and $^3P_1$ states. In Ba, these curve crossings may dominate so there is no appreciable Ba($^1P_1$)He molecular emission. We did not observe any $^3P_1 \rightarrow {}^1S_0$ emission but this is most likely due to transfer or radiative decay from the ^3P_J to the lower lying ^3D_J levels.

VII. NaHg Excimer

While investigating the SrHg system we observed strong fluorescence signals which were shown to be due to NaHg excimers, the Na being a contaminant at the time. The NaHg $A^2\Pi$-$X^2\Sigma$ band has been previously observed in a discharge tube. A sample cell is heated to 450°C to produce a Na pressure of 0.5 Torr and about 1000 Torr of Hg. An Ar^+ laser is used for excitation and fluorescence is detected by an optical multichannel analyzer.

Our interest in this system arose from the fact that we were producing NaHg excimers by laser excitation in the blue region of the spectrum, corresponding to the Na_2(X-B) absorption band. We observed strong Na_2 A-X and B-X emission and Na D line red wing emission which peaked at 6580 Å and was identified as NaHg emission. The intensity of Na_2 and NaHg emission was linear in the laser power and displayed a cell temperature dependence which scaled roughly as $[Na_2][Hg]$. Na D-line transition was also observed with an integrated intensity about 20% of that of the NaHg emission. However, when the Na 3s-3p transition was excited directly by a cw dye laser ($\sim$ 300 mW) no NaHg emission was observed. As the D-line resonance fluorescence was approximately 1000 times that observed when the dimers were excited, this rules out Na*(3p) as a direct intermediary in the reaction.

TABLE I : $^1P_1 \rightarrow {}^3P_J$ excitation transfer cross sections in units of $\mathring{A}^2$ for Calcium at 900°K and Strontium at 800°K. The estimated uncertainty in the cross sections is ± 25%.

	CALCIUM	STRONTIUM
He	0.025	0.38
Ne	0.028	0.61
Ar	0.046	1.6
Kr	0.064	1.4
Xe	1.15	0.25

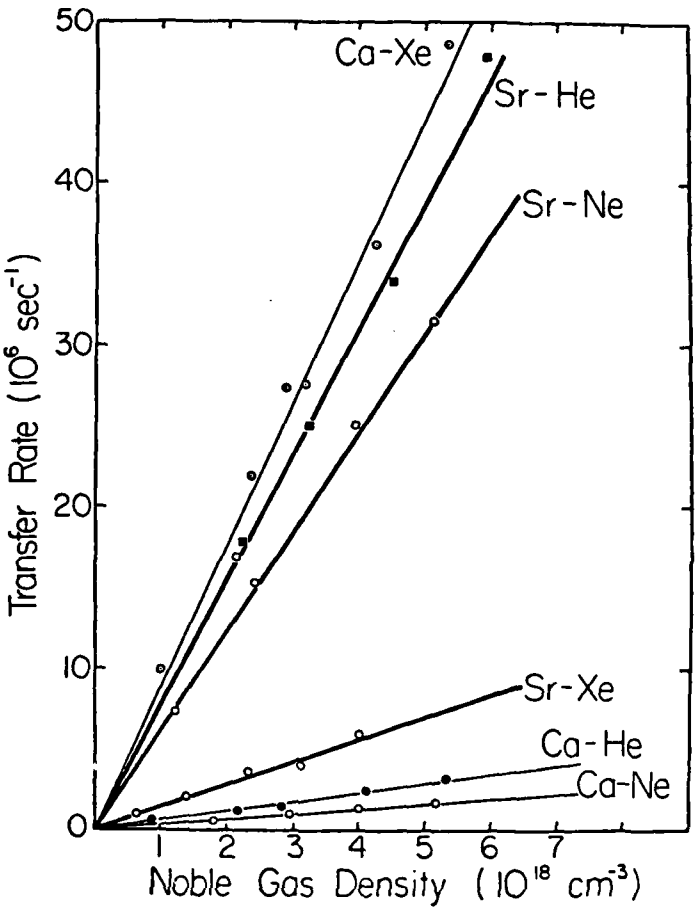

FIGURE 1
Plots Of ^1P - ^3P Transfer Rate vs
Noble Gas Density.

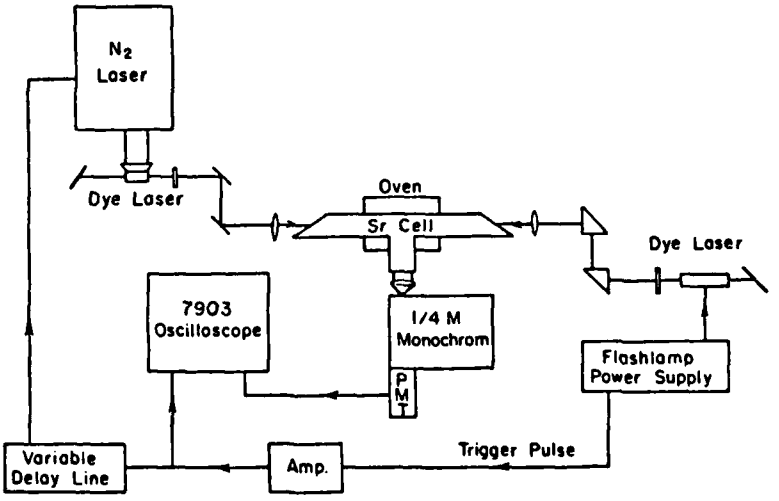

FIGURE 2
Schematic Of The Experimental Arrangement For
Determining the $^3P_1/^1S_o$ Population Ratio.

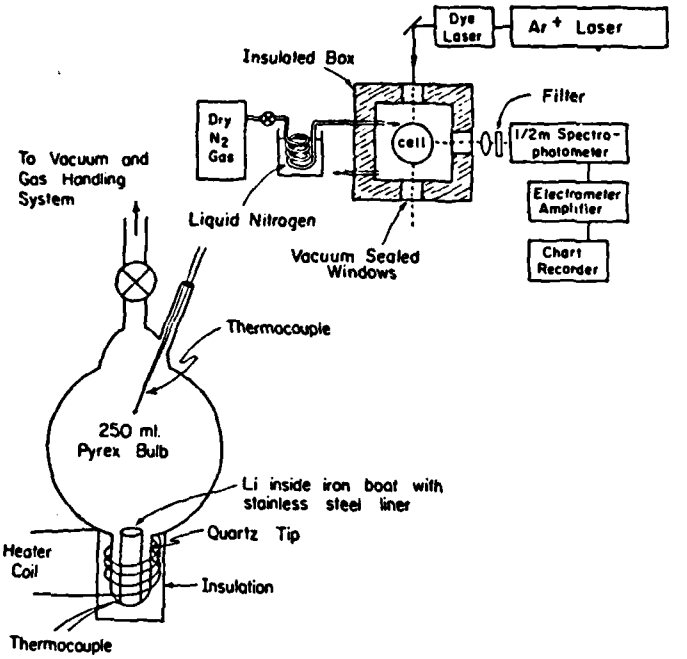

FIGURE 3
Basic experimental arrangement for measuring Na and Li-noble gas excimer fluorescence as a function of temperature.

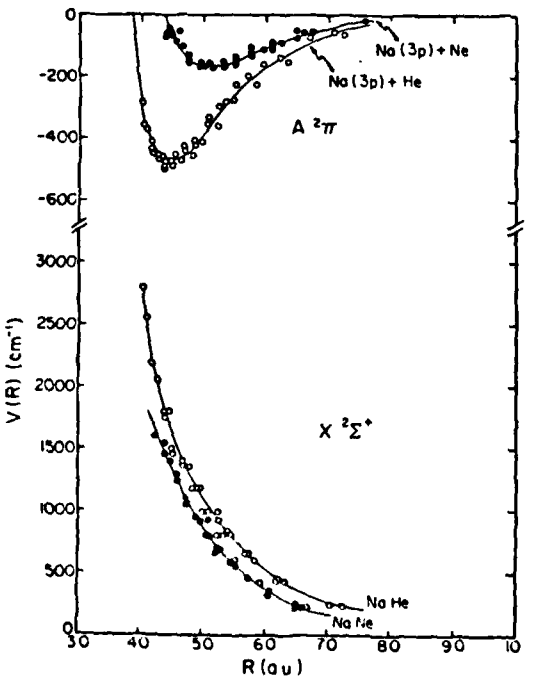

FIGURE 4
Experimentally determined $A^2\pi$ and $\chi^2\Sigma^+$ potentials for NaHe and NaNe.

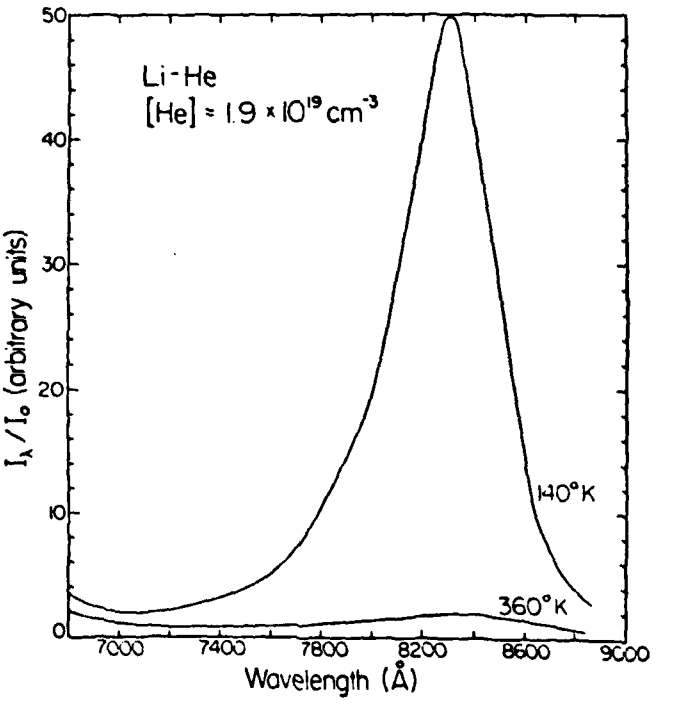

FIGURE 5
LiHe fluorescence spectra at 140°K and 360°K.